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RESEARCH MEMORANDUM

REACTION OF FLUORINE WITH CARBON AS A MEANS OF FLUORINE DISPOSAL

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SUMMARY

An experimental investigation has shown that amorphous carbon, such as wood charcoal, is readily applicable to fluorine disposal by the chemical reaction $C + F_2 \rightarrow CF_4$, C_2F_6, C_3F_8, C_4F_{10} . . . . The gaseous fluorocarbons formed are chemically inert and may be vented directly to the atmosphere. The method is simple and economical.

Fluorine and fluorine-oxygen and fluorine-nitrogen mixtures containing as little as 6.5 percent fluorine reacted spontaneously with fresh dry charcoal. Fluorine and fluorine-oxygen mixtures were consumed at rates up to 25 pounds per hour in an experimental portable reactor containing 6 cubic feet of charcoal. No rate limit was reached. Quantitative measurements of residual fluorine in the exhaust products ranged from 20.1 to a maximum of 77.5 parts per million.

Absorbed moisture in the charcoal may reduce efficiency to some extent. Even so, the product gases were very low in residual fluorine, as evidenced by only slight discoloration of potassium iodide indicator paper.

Although literature references have indicated that graphitized carbon can produce explosive carbon monofluoride by absorption of fluorine, no explosions were encountered in the present work with charcoal.

INTRODUCTION

Use of liquid or gaseous fluorine often involves disposal of small quantities of excess or residual material remaining in the system. Large quantities of fluorine may also be released in the event of refrigeration failure or by leakage in liquid-fluorine storage or transport containers.

The high toxicity of fluorine makes direct venting to the atmosphere inadvisable in most locations. Therefore, a method for safe, controlled, and efficient fluorine disposal is desirable. Current methods require

elaborate and expensive equipment, and most of them produce byproducts also requiring disposal treatment. These methods are:

(1) Reaction of gaseous fluorine with a caustic solution, followed by disposal of sodium fluoride with lime slurry (ref. 1)

(2) Direct burning of gaseous fluorine with fuels such as methane, followed by disposal of hydrogen fluoride (ref. 2)

(3) Reaction of gaseous fluorine with water vapor and subsequent disposal of hydrogen fluoride solutions (ref. 2)

(4) Reaction of gaseous fluorine with chlorides to release chlorine, which can be neutralized with a caustic solution (ref. 2)

(5) Reaction of gaseous fluorine with activated alumina, silica gel, or silicon carbide (investigated by the General Chemical Division, Allied Chemical and Dye Corp.)

A more desirable solution to the problem would be a simple and compact disposal unit in which fluorine would react spontaneously and produce relatively inert gaseous products that could be vented directly to the atmosphere.

The spontaneous reaction between carbon and gaseous fluorine $C + F_2 \rightarrow CF_4, C_2F_6, C_3F_8, C_4F_{10}$ . . . was investigated as a possible answer to the fluorine disposal problem (refs. 3 and 4). The product composition reported in references 3 and 4 suggests that the carbon-fluorine reaction consumes 5.7 pounds of fluorine per pound of carbon. Thus the weight of carbon required for a given fluorine disposal should be appreciably less than weights of reactants required by other methods.

Fluorocarbons generally are very stable because of the strong fluorine-carbon bond and can be decomposed only with difficulty. These gaseous products are chemically inert and nontoxic. For example, fluoroform and 2,2-difluoropropane are so stable that they may be substituted for nitrogen in air, and guinea pigs can exist for several hours without apparent harmful effects (ref. 5).

References 3, 4, and 6 report that graphite reacts with gaseous fluorine to form an unstable compound, carbon monofluoride. This compound is formed by absorption and chemical reaction at less than combustion temperature and explodes when heated in a fluorine-rich atmosphere. However, references 6 and 7 state that amorphous carbons, such as charcoal and lampblack, burn in fluorine to produce carbon tetrafluoride; and these references report no explosions. It appeared possible, therefore, that some forms of carbon may be spontaneously reacted with fluorine under controlled conditions to produce inert fluorocarbons.

The purpose of this investigation was to determine the feasibility of utilizing such a reaction for fluorine disposal. Pure fluorine and fluorine-nitrogen and fluorine-oxygen mixtures were passed through charcoal-charged reactors at various flow rates, concentrations, and run times. The reaction products were tested for fluorine content by a potassium iodide indicator paper and by chemical analysis.

PRELIMINARY EXPERIMENTS

In order to determine the reaction characteristics, small samples of wood charcoal were exposed to a stream of fluorine gas in a test tube (fig. 1). The reactions were spontaneous at room temperature, and the charcoal burned with a bright glow, the intensity of which depended upon the rate of fluorine flow. The combustion was easily controlled and proceeded very smoothly. Fluorine flow could be increased until the glass container fused and reacted with the fluorine. The outlet gases were tested for residual fluorine with potassium iodide indicator paper sensitive to 25 parts fluorine per million parts of gas (ref. 8). Occasionally a trace of fluorine was present at the start of a run, possibly because of absorbed moisture in the charcoal; after the reaction was established, no residual fluorine was detected. Water-saturated charcoal was not spontaneously reactive with fluorine; but, when ignited, it burned with a green flame and gave off a strong odor of hydrogen fluoride. High fluorine content was indicated in the product gases.

In order to simulate a practical carbon-fluorine reactor, the laboratory-scale apparatus shown in figure 2 was devised to eliminate direct contact of the reaction zone with any part of the reactor wall. The inlet was at the top of the vessel and the fluorine stream was injected into the center of the charcoal bed. The reaction zone was supported by the surrounding unreacted charcoal. Most of the heat was dissipated to the reactor wall adjacent to the reaction zone and above it, while the outlet gases remained relatively cool. Although the apparatus was successful in principle, a need for further protection of the reactor wall was indicated.

Some of the tests were repeated using graphitized carbon, which was not spontaneously combustible with fluorine at room temperature. The same results were obtained, except that a reaction initiator was required. A small piece of wood charcoal was used as the initiator.

Coal was the third material to be tested in this manner. An available sample of bituminous coal with the following approximate composition was used:

Substance	Concentration, percent
Carbon	84
Oxygen	5 to 6
Hydrogen	4 to 5
Nitrogen	1.0
Sulfur	0.6
Volatiles	18 to 20
Moisture	4 to 10

Reaction characteristics of the coal with fluorine were similar to those of charcoal. The reaction was spontaneous at room temperature and proceeded very smoothly. As in the case of charcoal, the fluorine reacted completely at the point of impingement on the surface of the sample. The heat from the reaction drove the volatiles from the unreacted coal. These volatiles condensed on the cool surfaces of the container outlet. However, this might be reduced to some extent by using a high-carbon, low-volatile-content anthracite coal.

These preliminary tests indicated the feasibility of using carbon for fluorine disposal. Of the carbon types tried, wood charcoal appeared to be most suitable.

APPARATUS AND PROCEDURE

In order to utilize the carbon-fluorine reaction in a practical disposal unit, a method for preventing the high-temperature reaction zone from burning through the reactor wall was required. Three stainless steel reactor configurations were tested.

Reactor 1 was a water-jacketed pipe, 2.0 inches in diameter and 30 inches long and was loaded with 0.05 cubic foot of charcoal (fig. 3). Its purpose was to determine whether water cooling would prevent fluorine from burning the metal container near the reaction zone. This reactor utilized a tangential-feed inlet at the top.

Reactor 2 was a graphite-lined pipe, 2 inches in diameter and 24 inches long. Inlet gases were fed vertically into the top and impinged directly onto 0.02 cubic foot of charcoal (fig. 4).

Reactor 3 was 30 inches in diameter and 26 inches deep (fig. 5) and was loaded with 6 cubic feet of charcoal. The design was based on information from preceding work and included the following features:

(1) A vertical injector which impinged the fluorine directly onto the charcoal surface

(2) An inner liner of suitable material to eliminate excessive temperature of the metal reactor wall

(3) A means of preventing the inlet gas from channeling along the reactor wall surface

Direct impingement of the inlet gases on the charcoal bed was considered desirable for localizing the reaction zone and minimizing contact with the reactor wall. Two materials were considered for the inner liner

of the reactor, refractory firebrick and carbon brick. Firebrick was used because of its ready availability. It was tested in a fluorine atmosphere and found to be resistant to fluorine at room temperature. At the carbon-fluorine combustion temperature some reaction occurred and caused reddish-brown streaks in the brick. The amount of reaction was considered to be negligible.

To prevent fluorine from channeling along the reactor wall, the firebrick was placed in a 24-inch-diameter circle. This left a 2-inch annular space between the liner and the outer shell. The reactor was completely filled, including the annular space, with ungraded crumbled charcoal (average particle size, approximately 0.5 cu in.). The lid of reactor 3 was modified to incorporate a water jacket after a number of runs indicated the need for it; the modified reactor is referred to as reactor 3A.

Pure fluorine and fluorine-nitrogen mixtures were fed into the reactors through a flow system consisting of (1) rotameters for continuous indication of flow rates and composition and (2) a pressure tank for preparing mixtures. A schematic diagram of this apparatus is shown in figure 6. For continuous operation fluorine and nitrogen were regulated through separate rotameters and fed directly to the reactor. For batch operation the rotameters were bypassed and only the pressure tank was used. The gas temperatures and partial pressures were measured, and a known quantity and concentration of each gas mixture was prepared.

The reaction products were tested qualitatively for residual fluorine content with potassium iodide indicator paper. Quantitative analyses were made by absorbing known volumes of exhaust products and reacting them with potassium iodide solutions. A sampling manifold was connected to the reactor exhaust pipe. Six sampling units (one is shown schematically in fig. 7) were attached to the manifold so that consecutive or simultaneous samples could be obtained. These samples, collected at a uniform rate during each run, were titrated with an acidified solution of sodium thiosulfate and starch. The average molecular weight of the exhaust gases was calculated from composition data reported in references 3 and 4, from which the weight compositions in parts per million were evaluated.

RESULTS AND DISCUSSION

Experimental results are shown in table I.

Five runs were made with the water-jacketed reactor 1 filled with charcoal to a depth of 25 inches. The reactions proceeded smoothly, and no reactor-wall burnouts occurred. However, residual fluorine was indicated in the exhaust products in all five runs (table I(a)). This was

attributed to the channeling of fluorine between the charcoal and the cold metal surface of the reactor wall, which was especially probable in these tests, since the fluorine was injected into the reactor tangentially.

In reactor 2 a protective graphite liner was substituted for the water jacket, and a vertical injector impinged the fluorine directly on the charcoal surface. The inner liner was equally as effective as water cooling in preventing wall burnouts, and with only a 10-inch-deep layer of charcoal in the reactor, no fluorine was indicated in the effluent until the charcoal was exhausted (table I(a)).

A series of runs was made using reactors 2 and 3 with fluorine and fluorine mixtures under controlled conditions. Fluorine content of the input gases ranged from 6.5 to 100 percent; feed rates into the reactors were varied from 0.5 to 21.1 pounds per hour with run durations up to 5 minutes.

Variation of input fluorine concentration had no observed influence on the residual fluorine content in the effluent (table I(a)). Reactions were spontaneous, smooth, and nonexplosive during all tests, even those employing the most dilute mixtures.

During runs 12 to 16 (reactor 3) higher fluorine concentration in the effluent was indicated. Upon inspection, a considerable amount of water was found to have leaked into the reactor from an external water spray. No other cause for this decreased disposal efficiency was found, and the results returned to normal when the reactor was recharged with fresh dry charcoal.

The data of table I(a) show a slight increase in indicator coloration with increasing flow rates and longer run times. Since coloration of the indicator paper is accumulative with time and occurs more rapidly at higher effluent flow rates, the relation between feed rate and effluent composition was obscure for these runs.

Quantitative determinations of the fluorine content in the effluent gases are listed in table I(b) for the final series of tests. These runs were made with pure fluorine at some of the highest feed rates of the experimental work. The highest fluorine concentration found in the effluent was 77.5 parts per million, using charcoal containing absorbed moisture. Comparison of quantitative data with qualitative observations throughout the investigation indicates that fluorine concentrations lower than 50 parts per million in the effluent gases were generally attained. While feed rates near 25 pounds per hour were thus handled successfully, no upper limit on feed rate was established.

The data, listed chronologically in table I(b), appear to show a trend toward decreased efficiency of the reactor with time. It was not determined whether this effect might be attributed to a poisoning of the charcoal bed by reaction products.

In an actual fluorine disposal application, reactor 3 containing 6 cubic feet of charcoal consumed pure fluorine at a rate of 12.5 pounds per hour continuously for a period of 2 hours; in addition, a mixture containing 10 to 15 percent of fluorine in oxygen was successfully disposed of at an average rate of 16.1 pounds per hour for 30 minutes (table I(c)).

Over 150 pounds of fluorine have been consumed safely by reaction with wood charcoal. No explosions were encountered in any phase of this work, although wide ranges of conditions were imposed on the systems. It is felt that explosion hazards are avoided by maintaining spontaneous-reaction conditions.

SUMMARY OF RESULTS

The following results have demonstrated the feasibility of using a carbon-fluorine reaction to dispose of excess fluorine:

1. Fluorine and fluorine-oxygen and fluorine-nitrogen mixtures containing as little as 6.5 percent fluorine reacted with charcoal spontaneously and burned nonexplosively.

2. Fluorine was consumed satisfactorily in an experimental portable reactor containing 6 cubic feet of charcoal at rates as high as 25 pounds per hour. No rate limit was reached.

3. Residual fluorine content in the exhaust products was generally less than 50 parts per million; therefore, direct venting to the atmosphere was acceptable. Quantitative measurements ranged from 20.1 to a maximum of 77.5 parts per million.

4. Water in the charcoal appeared to reduce disposal efficiency.

CONCLUDING REMARKS

Wood charcoal provides an economical and easily controlled method for fluorine disposal. It should be noted, however, that the limitations of this method of fluorine disposal have not been fully explored. Further work is required to determine:

(1) Feed rate limitations

(2) The effects of absorbed moisture content on disposal efficiency

(3) The minimum fluorine concentration in inert gases or oxygen that will react spontaneously and nonexplosively with charcoal

(4) The possibility of charcoal-bed poisoning occurring with extensive use of the reactor

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, May 3, 1957

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TABLE I. - DATA FROM [illegible] EXPERIMENTS

(a) Qualitative results.

Reactor	Run	Entering gas: Composition: Fluorine, percent	Entering gas: Composition: Diluent	Entering gas: Flow rate, lb/hr	Total flow time, min	Color of indicator paper (a)	Remarks	
1, water-jacketed pipe ([illegible] cu ft of charcoal)	1	100	None	1 to 5	---	Yellow to black	Immediate coloration of indicator paper	
	2				---			
	[illegible]				---			
	4				---			
	[illegible]				---			
2, Graphite-lined pipe ([illegible] cu ft of charcoal)	[illegible]	[illegible]	Nitrogen	1.5	[illegible]	White		
	[illegible]	41.5		1.0	[illegible]			
	[illegible]	[illegible]		.7	4.0			
	[illegible]	[illegible]		2.0	7.0			
	[illegible]	[illegible]		.5	[illegible]			
	11	[illegible]		2.5	[illegible]	Yellow	Charcoal content became exhausted	
3, Fluorothene-lined reactor ([illegible] cu ft of charcoal)	12	100	None	----	---	Black		
	13	100	None	----	---	Black		
	14	100	None	----	---	Black		
	15	[illegible]	Nitrogen	13.4	[illegible]	Black	Gradual color to black at 120 sec	Water leaked into reactor from external source
	16	[illegible]		12.2	[illegible]	Yellow to black	Yellow [illegible] sec	
	17	100		[illegible]	[illegible]	White	Low flow rate; short to moderate run time	
	18	[illegible]		[illegible]	[illegible]			
	19	[illegible]		4.0	[illegible]			
	[illegible]	[illegible]		6.6	[illegible]			
	[illegible]	[illegible]		6.5	[illegible]			
	[illegible]	12.4		[illegible]	[illegible]			
	[illegible]	[illegible]		6.2	[illegible]			
	24	100	None	12.1	[illegible]		High flow rate; short run time	
	[illegible]	[illegible]	Nitrogen	15.6	[illegible]			
	[illegible]	[illegible]	Nitrogen	9.6	[illegible]			
	[illegible]	[illegible]	None	[illegible]	[illegible]	Yellow	Color at [illegible] sec	High flow rate; moderate run time
	[illegible]	[illegible]	None	9.1	[illegible]		Gradual color to brown at [illegible] sec	
	[illegible]	[illegible]	Nitrogen	[illegible]	[illegible]		Color at 60 sec	
	[illegible]	[illegible]		10.0	[illegible]		Gradual color to brown at [illegible] sec	
	[illegible]	[illegible]		15.0	[illegible]		Color at end of run	
	[illegible]	[illegible]		15.1	[illegible]		Color at 60 sec	
	[illegible]	[illegible]		12.5	[illegible]	White		
	34	[illegible]		14.4	[illegible]	Yellow	Color at [illegible] sec	

[a] Color change: White → Yellow → Brown → Black (increasing fluorine content).

TABLE I. - Concluded. DATA FROM FLUORINE DISPOSAL EXPERIMENTS

(b) Quantitative results.

Reactor	Run	Entering gas			Total flow time, min	Color of indicator paper (a)	Fluorine found in effluent by chemical titration, parts per million	Remarks
		Composition		Flow rate, lb/hr				
		Fluorine, percent	Diluent					
3A, Firebrick-lined reactor with water-jacketed lid (6 cu ft of charcoal)	35	100	None	14.0	15.0	White	----	Fresh dry charcoal (about 2 to 3 percent H_2O)
	36			15.0	5.0	White	25.8	Carbon exposed to cold, wet atmosphere for 1 week prior to these runs
	37			13.5		White	34.5	
	38			10.6		Brown	40.3	
	39			4.4		Brown	43.1	
	40			5.4		Dark brown	54.6	
	41			23.0		Black	77.5	
	42			15.0	10.8	White	20.1	Fresh dry charcoal
	43			7.2	6.5	-----	28.7	
	44			23.5	2.8	-----	23.0	
	45			5.2	7.3	-----	28.7	
	46			13.8	4.0	-----	48.8	
	47			19.5	2.8	-----	51.7	
	48			24.6	8.3	-----	43.1	

(c) Results from field operation.

Reactor	Run	Entering gas			Total flow time, min	Remarks
		Composition		Flow rate, lb/hr (b)		
		Fluorine, percent	Diluent			
3, Firebrick-lined reactor (6 cu ft of charcoal)	A	100	None	12.5	120	Slight odor[c] of "burned plastic" noted at times from distance of 8 ft
	B	10 to 20	Oxygen	26.5	90	Slight odor at end of run (because of leak in reactor lid gasket)
	C	100	None	6.0	30	No odor at any time

[a]Color change: White $\xrightarrow{\text{(Increasing fluorine content)}}$ Black.

[b]Average over-all values; rates at start of run were appreciably higher.

[c]Sensitivity of smell to fluorine is approximately 3 parts per million (data obtained from Public Health Service).

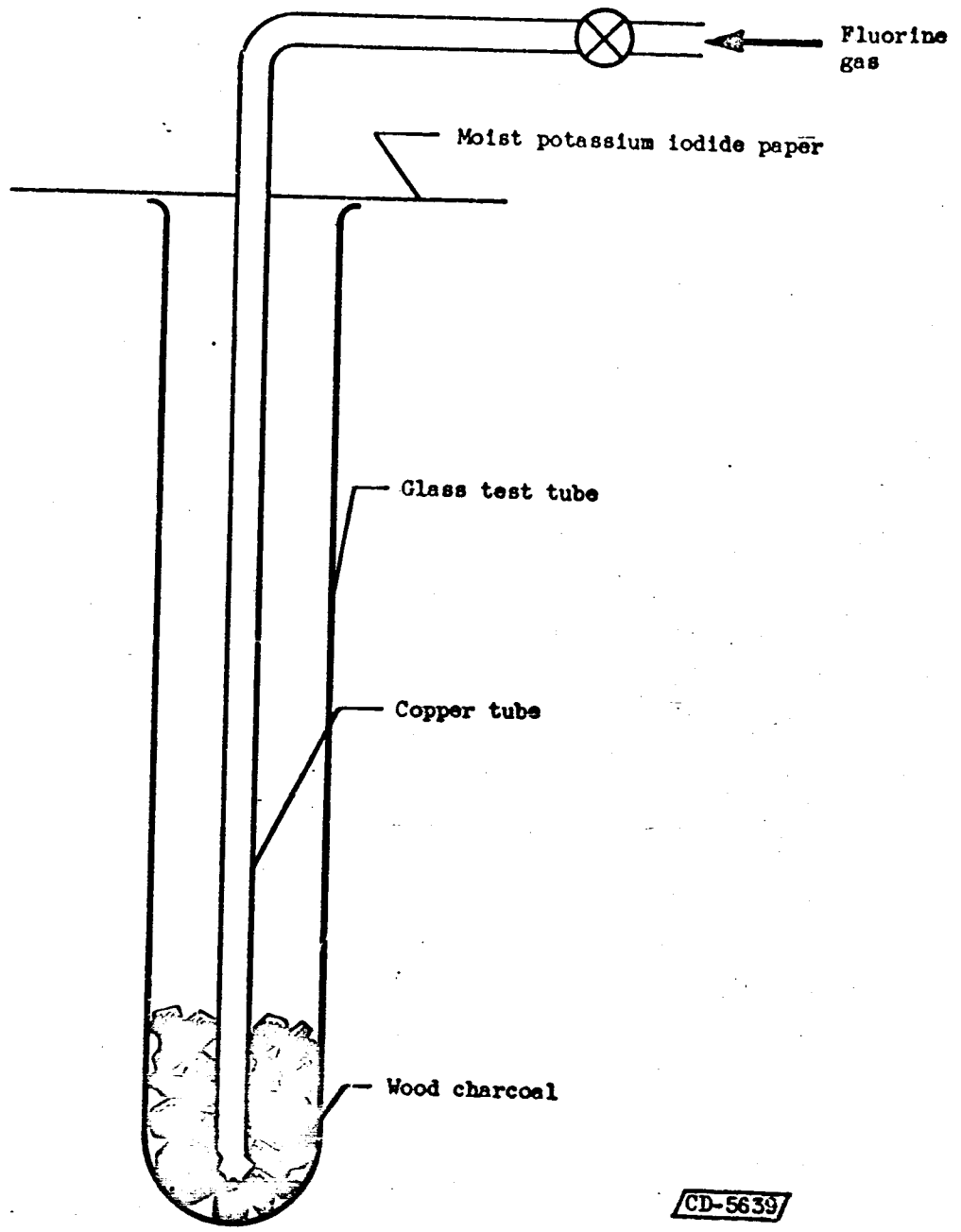

Figure 1. - Laboratory setup for observing reaction characteristics of fluorine with carbon.

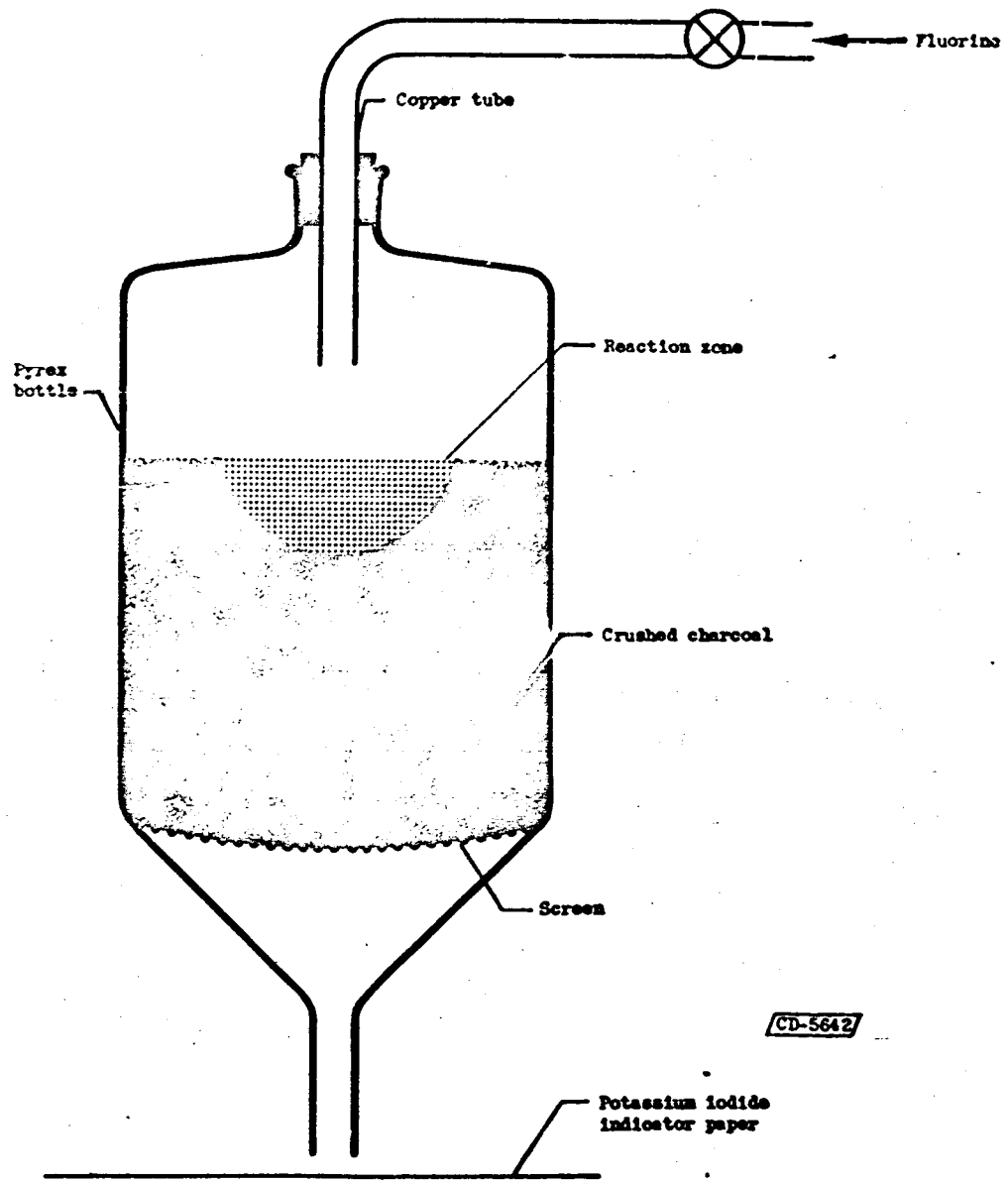

Figure 2. - Laboratory reactor with top inlet feed and isolation of reaction zone by unreacted charcoal.

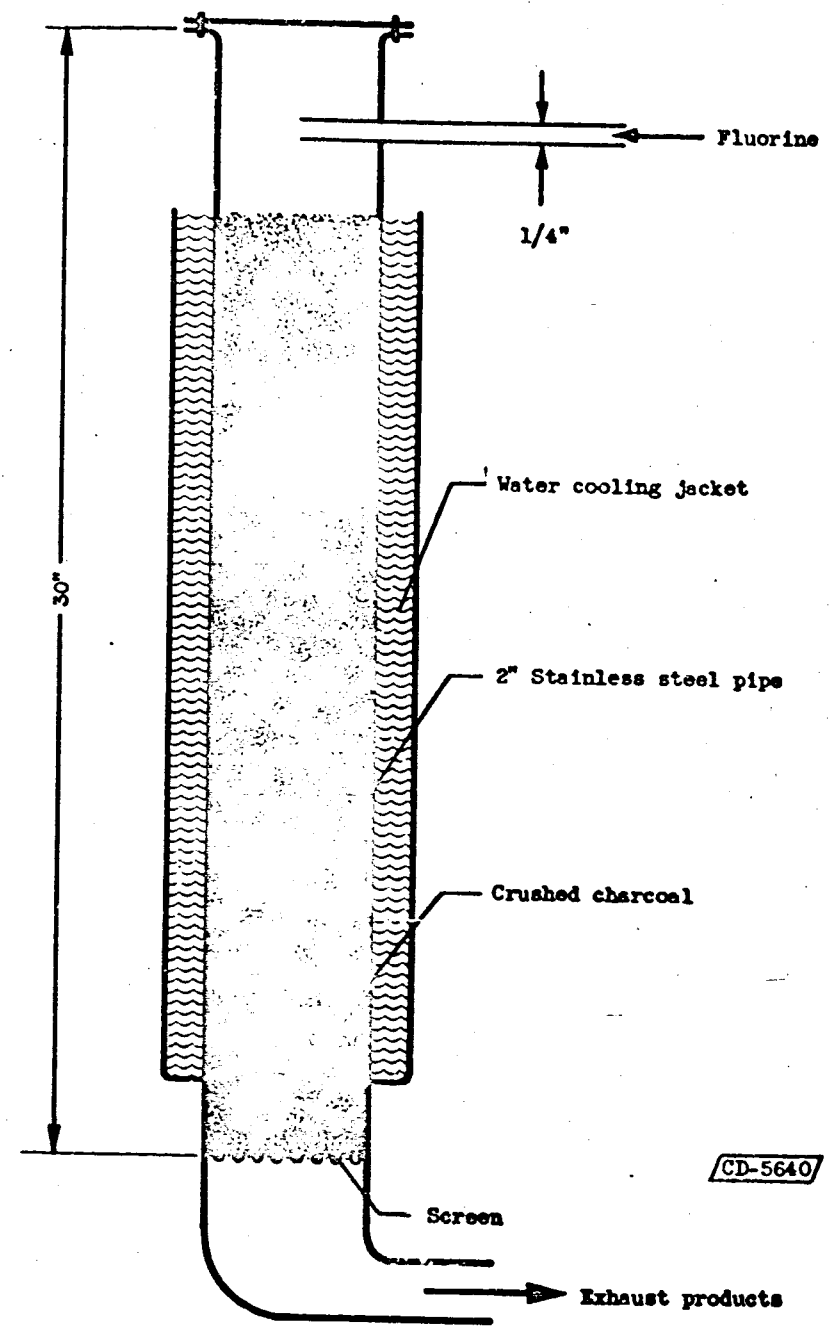

Figure 3. - Reactor 1. Water-jacketed reactor with tangential-feed inlet.

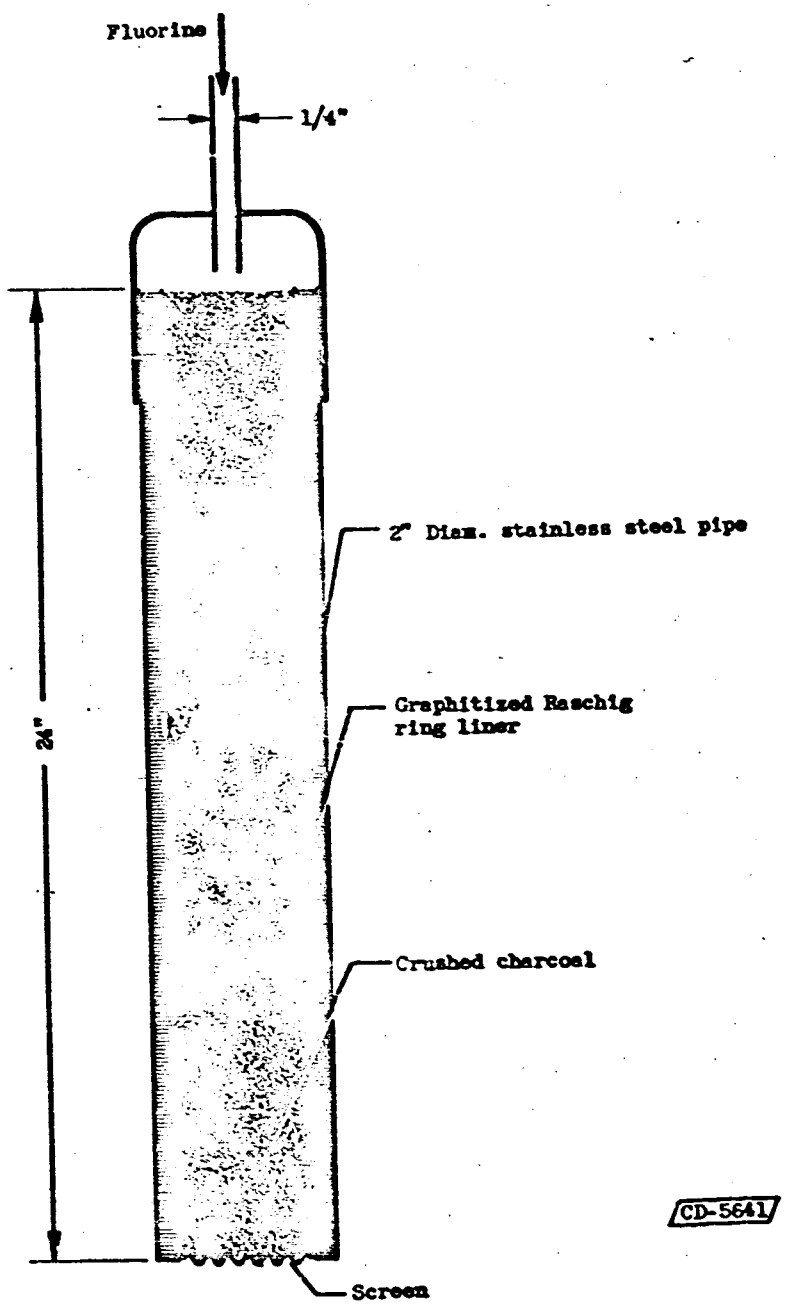

Figure 4. - Reactor 2. Carbon-lined reactor with direct-vertical-feed inlet.

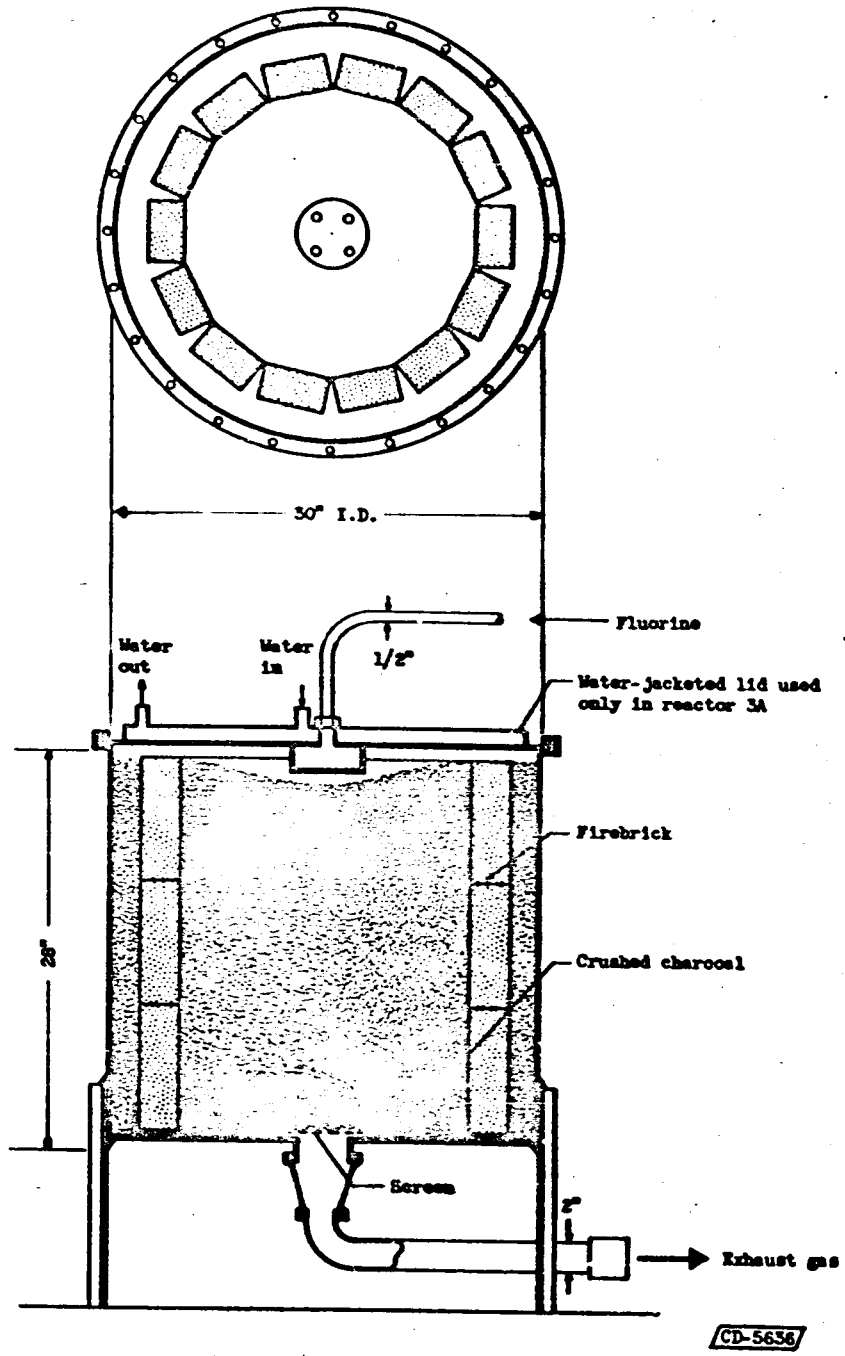

Figure 5. - Reactor 3. Firebrick-lined reactor used in final tests and in actual field disposal of fluorine.

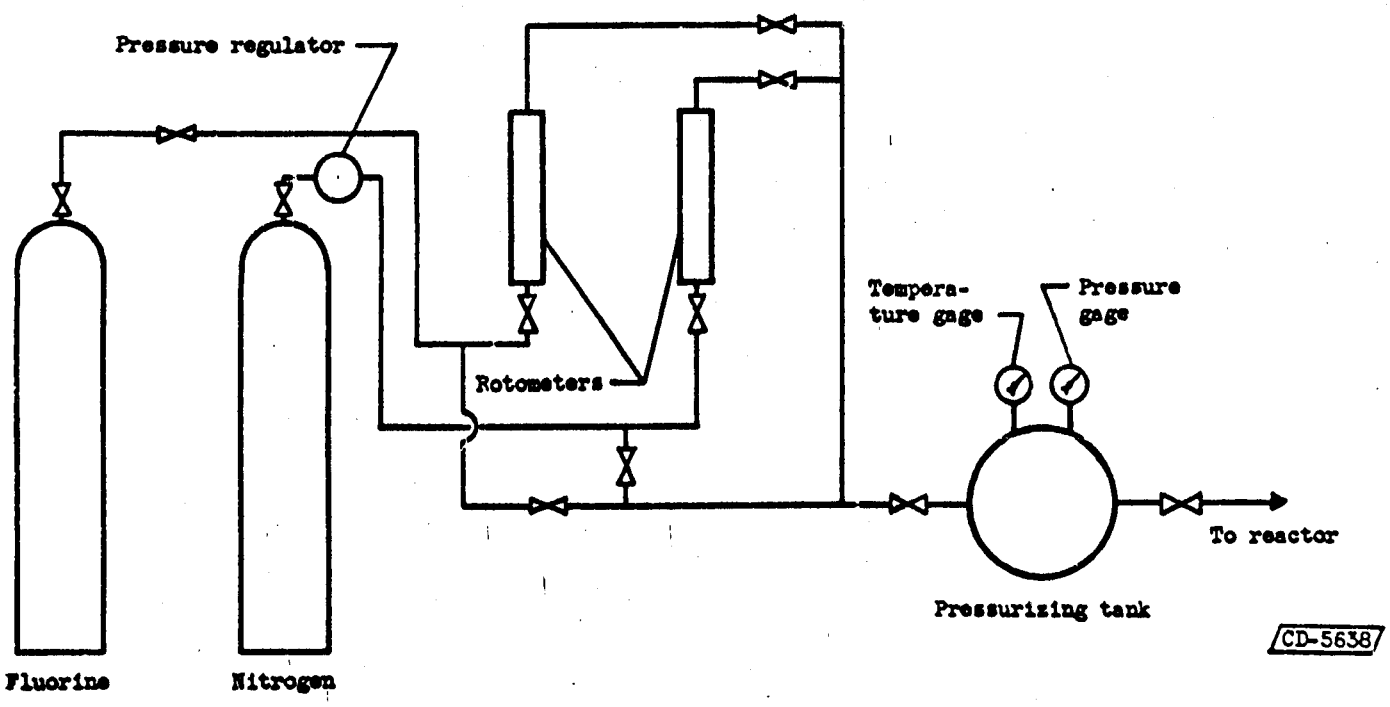

Figure 6. - Apparatus for supplying reactor feed at controlled rate and composition.

NACA RM E57E02

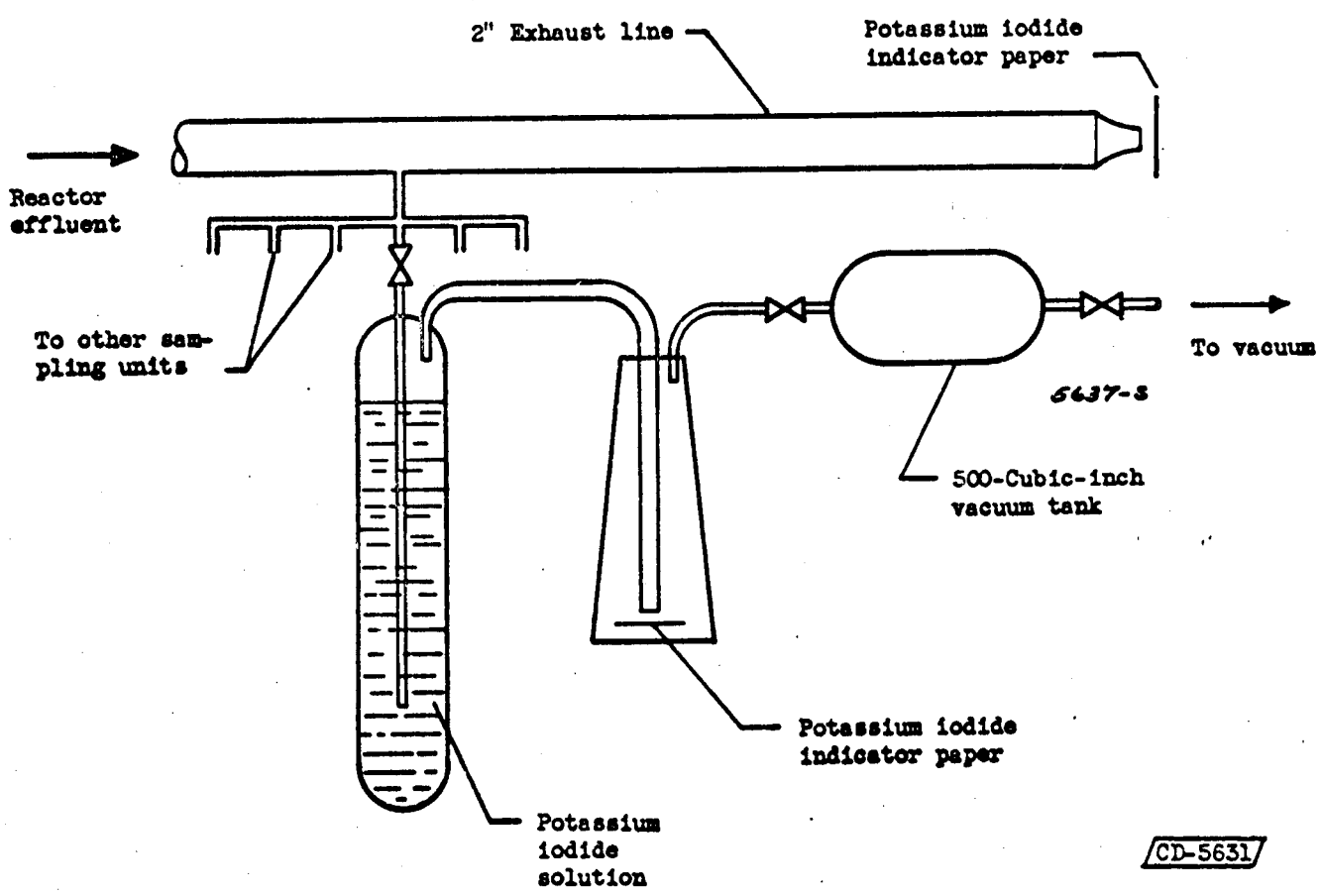

Figure 7. - Unit for sampling effluent gases from reactor.